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(6) Metal Template Syntheses of Porphin and
Tetraazaannulenes.

by

(10) Paul V. Roling ~~and~~ Minoru Tsutsui

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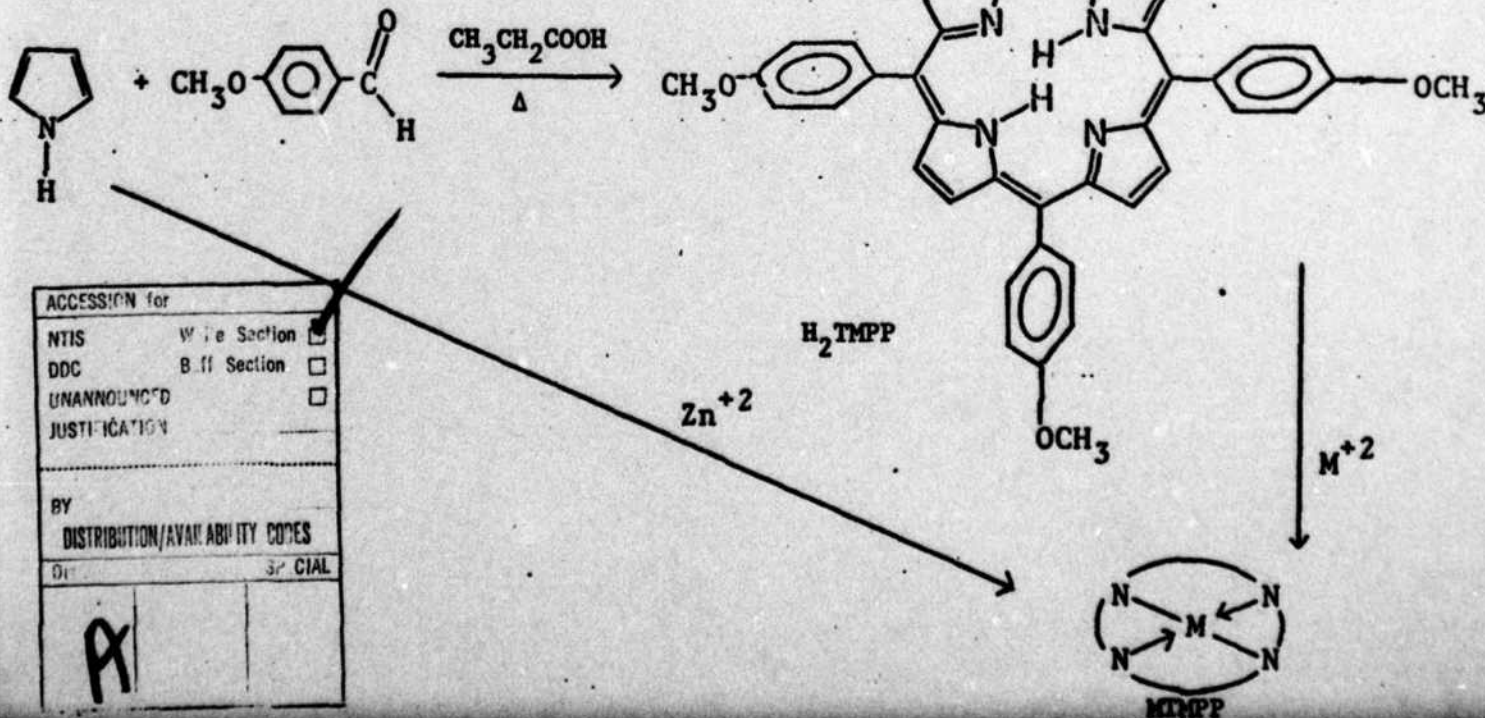
Metal Template Syntheses of Porphin and Tetraazaannulenes

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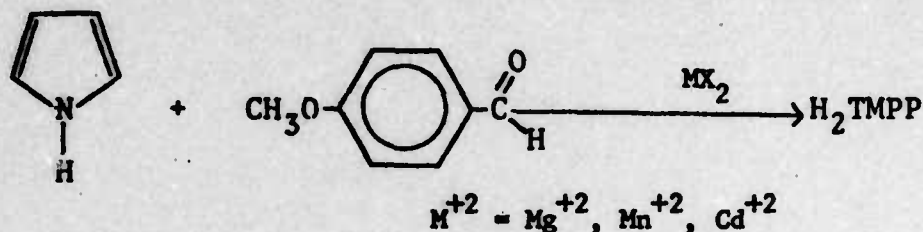
Metallophthalocyanines, metalloporphins, and metallotetraazaannulenes are important as biological models for oxygen complexation, as potential fuel cell catalysts and as tumor localizers to name a few uses. However, their synthesis in high yields is still an area of continuing research.

Many metallophthalocyanines can be formed by tetramerization of phthalonitrile with metal or metal salt. Numerous metals and metal salts can be used.¹ The metalloporphins, on the other hand, are synthesized from the porphin and a metal salt.² Only a few reports exist of the synthesis of a metalloporphin directly from a pyrrole, an aldehyde, and a metal salt.^{3,4} These reports utilize zinc salts as catalysts, but made no mention of other metal salts as possible catalysts or templates. Prompted by these



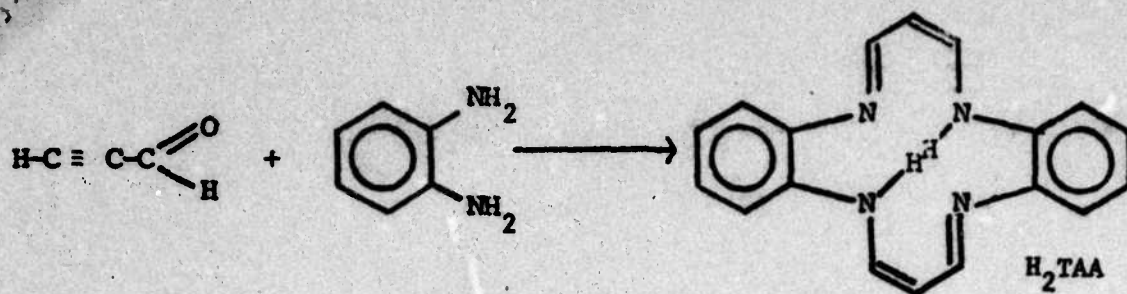
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reports we attempted to use other metal salts to template the reaction of pyrrole and p-anisaldehyde to give the metal tetra(p-methoxyphenyl)porphin (MTMPP). The method of Adler et al.⁵ was used with the addition of a metal salt to the reaction. The results are listed in Table 1. As can be seen d^0 , d^5 ,

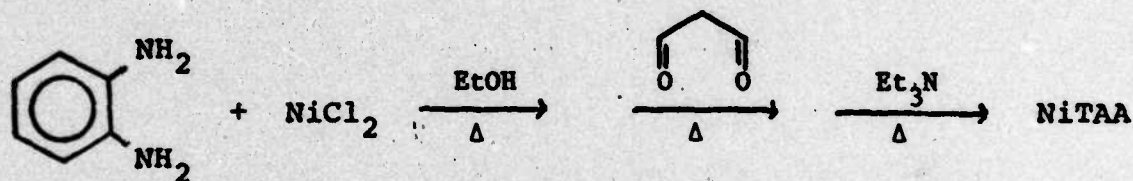


and d^{10} metal ions, except Fe^{+3} , gave porphins whereas, d^7 , d^8 , and d^9 metals gave only black powders. On isolation of the porphins only zinc was found to be incorporated into the porphin, while magnesium, manganese, and cadmium were not incorporated. (These metal ions are not commonly incorporated in an acidic medium.²) This leaves open the question of whether templation occurred or not for the d^0 , d^5 , and d^{10} ions. Two possibilities can be conceived: (1) templation by the metal followed by metal ion removal from the porphin or (2) no participation by the metal at all. Since no increase in yields occurred, possibility (2) in our opinion seems favored. Chromatography of the black powders showed no free porphin or metalloporphin to be present. In two instances, Cu^{+2} and Ni^{+2} , the black powders were decomposed to give a very small yield of metalloporphin, thus indicating that some porphin may be present but in a complexed form. This means that the d^7 - d^9 metals have catalyzed a side reaction, which normally without the metal is small to nonexistent.

Metallotetraazaannulenes (MTAA) are formed by the reaction of propargyl aldehyde and o-phenylenediamines, with or without a metal salt.⁶ The health hazard of propargyl alcohol,⁷ from which the aldehyde is made, and the instability of the aldehyde,⁸ made us look for another route to the MTAA's.



Templation by cobalt and copper salts of o-phenylenediamine and bromomalondialdehyde to give dibromo MTAA's,⁹ prompted us to explore reactions of malondialdehyde in place of the bromo compound. On reacting the o-phenylenediamine nickel complex with malondialdehyde and subsequent treatment with triethylamine, NiTAA was obtained. The yield was about half that of the above method.⁶ A similar experiment, but without triethylamine, failed to give any NiTAA, as previously reported.¹⁰



The use of cobalt, copper, and zinc chlorides gave no detectable MTAA. Since the nickel cannot presently be removed, the reaction is limited in use.

Experimental

Visible spectra were recorded on a Beckmann 24 Spectrophotometer. The alumina used was Fisher's Alumina-Absorption and had an activity of about 2.

meso-Tetra(p-methoxyphenyl)porphin (H_2TMPP). A typical example is given: Pyrrole (1.4 ml, 20 mmol), 2.4 ml (20 mmol) of p-anisaldehyde, 4.3 g (22 mmol) of manganese chloride tetrahydrate, 5.0 g (51 mmol) of potassium acetate (this is not used when the metal acetate was available), and 100 ml of propanoic acid were refluxed for 30 min. The reaction mixture was then cooled to room temperature, filtered, and the purple crystals washed with 300 ml of methanol.

The crystals were air dried to give 0.55 g (14%) of *meso*-tetra(p-methoxyphenyl)-porphin. The visible spectrum was identical with that of authentic H_2 TMPP and not that of MnTMPP.

Other results are listed in Table 1.

Copper *meso*-tetra(p-methoxyphenyl)porphin(CuTMPP): Black solid, from the above reaction with cupric acetate, (2.0 g) and 8.0 g (31 mmol) of iodine in 150 ml $CHCl_3$ were stirred for 22 hrs. A saturated solution of sodium thiosulfate (50 ml) was added, stirring continued for 10 min, and the layers separated. The $CHCl_3$ layer was chromatographed on 75 g of alumina. Elution with $CHCl_3$ eluted an orange band, which was evaporated and the resulting solid washed with 300 ml of methanol to give 10 mg (3% based on pyrrole) of purple crystals of CuTMPP. The visible spectrum was identical with that of authentic CuTMPP.

A similar treatment of the black solid from a nickel reaction gave but a trace of NiTMPP.

Nickel tetraazaannulene(NiTAA): Nickel chloride hexahydrate (3.0 g, 13 mmol), 2.6 g (25 mmol) of o-phenylenediamine, and 100 ml of absolute ethanol were refluxed for 30 min (a gray precipitate resulted). To this solution was added malondialdehyde (25 mmol, made by stirring 4.4 ml of 1,1,3,3-tetramethoxypropane, 4.4 ml of water, and 0.2 ml of concentrated hydrochloric acid until the solution was homogeneous -- about 5 min.). The reaction mixture immediately turned reddish in color. Refluxing was continued for 2 hrs, at which time 3.9 ml (28 mmol) of triethylamine was added and refluxing was continued for an additional 21 hrs. The reaction was then allowed to cool to room temperature and was filtered. The solid was extracted fourteen times with 100-ml portions of boiling chloroform. The chloroform extracts were placed on a column of 500 g alumina and elution with chloroform removed an orange band (a few other small bands that were very slow moving with chloroform were not further investigated). Evaporation to

almost dryness gave 0.40 g (9%) of purple-red crystals of NiTAA; mp > 340°, the visible spectrum was identical with that of Hiller et al.⁶

Replacement of nickel chloride with cobalt chloride, cupric chloride, or zinc chloride failed to give any MTAA.

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TABLE I

Results of the Porphin Template Synthesis

MX ^a	Resulting ^b MTMPP	% Yield of MTMPP
none	H ₂ TMPP	22
MgCl ₂	H ₂ TMPP	14
MnCl ₂	H ₂ TMPP	14
FeCl ₃	none	(.36) ^c
Fe(OAc) ₃	none	(1.11) ^c
Co(OAc) ₂	none	(.64) ^c
Ni(OAc) ₂	none	(.44) ^c
Cu(OAc) ₂	none	(1.79) ^c
ZnCl ₂	ZnTMPP	8
CdCl ₂	H ₂ TMPP	18

^a If X = Cl then KOAc was added to buffer the HCl formed. cf. Experimental

^b As determined by the visible spectra.

^c A black powder was all that could be found. Chromatography of the black powder showed no TMPP. The numbers in parentheses represent the ratio of g of black powder to g of pyrrole used.

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